

Upper limits on CH₃OH in the HD 163296 protoplanetary disk

Evidence for a low gas-phase CH₃OH/H₂CO ratio

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ABSTRACT

Context. Methanol (CH₃OH) is at the root of organic ice chemistry in protoplanetary disks. Its connection to prebiotic chemistry and its role in the chemical environment of the disk midplane makes it an important target for disk chemistry studies. However, its weak emission has made detections difficult. To date, gas-phase CH₃OH has been detected in only one Class II disk, TW Hya.

Aims. We aim to constrain the methanol content of the HD 163296 protoplanetary disk.

Methods. We use the Atacama Large Millimeter/submillimeter Array (ALMA) to search for a total of four CH₃OH emission lines in bands 6 and 7 toward the disk around the young Herbig Ae star HD 163296. The disk-averaged column density of methanol and its related species formaldehyde (H₂CO) are estimated assuming optically thin emission in local thermodynamic equilibrium. We compare these results to the gas-phase column densities of the TW Hya disk.

Results. No targeted methanol lines were detected with Keplerian masking in the image plane nor with matched filter analysis in the *uv* plane individually or after line stacking. The 3 σ disk-integrated intensity upper limits are < 51 mJy km s⁻¹ for the band 6 lines and < 26 mJy km s⁻¹ for the band 7 lines. The band 7 lines provide the strictest 3 σ upper limit on disk-averaged column density with $N_{\text{avg}} < 5.0 \times 10^{11}$ cm⁻². The methanol-to-formaldehyde ratio is CH₃OH/H₂CO < 0.24 in the HD 163296 disk compared to a ratio of 1.27 in the TW Hya disk.

Conclusions. The HD 163296 protoplanetary disk is less abundant in methanol with respect to formaldehyde compared to the disk around TW Hya. Differences in the stellar irradiation in this Herbig Ae disk as compared to that of a disk around a T Tauri star likely influence the gaseous methanol and formaldehyde content. Possible reasons for the lower HD 163296 methanol-to-formaldehyde ratio include: a higher than expected gas-phase formation of H₂CO in the HD 163296 disk, uncertainties in the grain surface formation efficiency of CH₃OH and H₂CO, and differences in the disk structure and/or CH₃OH and H₂CO desorption processes that drive the release of the molecules from ice mantles back into the gas phase. These results provide observational evidence that the gas-phase chemical complexity found in disks may be strongly influenced by the spectral type of the host star.

Key words. astrochemistry – protoplanetary disks – submillimeter:stars

1. Introduction

Methanol is an astrobiologically relevant molecule because it acts as a precursor to more complex organic molecules (COMs) that may develop into amino acids and other building blocks of life (Öberg et al. 2009; Herbst & van Dishoeck 2009). Maintaining an understanding of methanol chemistry through the numerous stages of star and planet formation is essential to make predictions on the molecular complexity available for incorporation into extrasolar planetary bodies (e.g., Drozdovskaya et al. 2014). The CH₃OH molecule is regularly detected in the earlier, embedded stages of star formation both in the solid phase through ice absorption (Grim et al. 1991; Skinner et al. 1992; Dartois et al. 1999; Pontoppidan et al. 2004; Bottinelli et al. 2010; Kristensen et al. 2010; Shimonishi et al. 2010; Boogert et al. 2015) and in the gas phase (Friberg et al. 1988; van Dishoeck et al. 1995; Graninger et al. 2016; Lee et al. 2017). These observations pro-

vide evidence for the presence of CH₃OH ices in cold molecular clouds and protostellar envelopes.

To date, methanol has been detected in two protoplanetary disks: the Class II TW Hydrae (Walsh et al. 2016) and the younger Class I V883 Orionis, an outbursting FU Orionis object (van 't Hoff et al. 2018). There are currently few informative upper limits on gas-phase methanol in disks. The reason for the apparent absence of gas-phase methanol in protoplanetary disks is not immediately obvious because CH₃OH is expected to form via the hydrogenation of CO ices (Watanabe et al. 2003; Cuppen et al. 2009) on the surface of dust grains. Also, the colder, outer regions of protoplanetary disks are expected to inherit a reservoir of methanol ice formed earlier, during the protostellar or interstellar phase. Methanol is produced by the same grain surface formation pathway as formaldehyde, which is readily detected in disks (Aikawa et al. 2003; Öberg et al. 2010; Qi et al.

2013; van der Marel et al. 2014; Loomis et al. 2015; Öberg et al. 2017; Carney et al. 2017). However, because of the much higher methanol binding (desorption) energy (e.g., E_{des} of ~ 2000 K for H_2CO and ~ 5500 K for CH_3OH in mixtures of water ice; Collings et al. 2004; Garrod & Herbst 2006), methanol is expected to be frozen out over a much larger region of the disk than formaldehyde.

Variation in the formaldehyde and methanol content across protoplanetary disks may point to differences in their formation processes. Formaldehyde can be formed in the gas phase and on grain surfaces, therefore a lower than expected methanol-to-formaldehyde ratio could be due to a more efficient gas-phase pathway to form H_2CO (Fockenberg & Preses 2002; Atkinson et al. 2006), less efficient conversion of H_2CO into CH_3OH on grain surfaces than expected, or lower than expected CH_3OH photodesorption rates and/or immediate UV photodissociation of gas-phase CH_3OH (Bertin et al. 2016; Cruz-Díaz et al. 2016).

The HD 163296 (MWC 275) system is an ideal testbed for exploring chemical processing in protoplanetary disks, in particular for organics. It is an isolated Herbig Ae pre-main sequence (PMS) star with spectral type A2Ve at an age of ~ 5 Myr (Alecian et al. 2013). The star is surrounded by a large, bright protoplanetary disk containing a significant reservoir of gas that extends out to ~ 550 AU in the gas based on CO measurements (de Gregorio-Monsalvo et al. 2013). The disk has an inclination of 44° , a position angle of 133° , and a total mass of $M_{\text{disk}} \approx 0.09 M_\odot$ based on physical models (Qi et al. 2011; Rosenfeld et al. 2013). At such an inclination, the vertical structure as well as the radial structure can be inferred directly from the molecular line emission maps (Rosenfeld et al. 2013; Flaherty et al. 2015).

Recent measurements of the stellar parallax by Gaia put the HD 163296 system at a distance of $d = 101 \pm 1$ pc (Gaia Collaboration et al. 2018), significantly closer than previous distance estimates of 122 pc (van den Ancker et al. 1998).¹ While the new distance will affect the stellar parameters, this work adopts the previously reported values for stellar mass ($2.3 M_\odot$; Qi et al. 2011) and distance ($d = 122$ pc). The analysis presented here focuses on the disk-averaged molecular column density ratios of methanol and formaldehyde within the same disk. The column density is derived from the disk-integrated line flux, therefore the updated Gaia distance measurements will affect the line flux similarly for molecular species within the same disk, and the effect of the new distance is canceled out.

The proximity and size of the disk combined with the high total luminosity of the Herbig Ae PMS star provides a unique opportunity to fully resolve the location of the CO snow line, i.e., the midplane radius beyond which gas-phase CO will freeze out into ice (Qi et al. 2011; Mathews et al. 2013; Qi et al. 2015). Current estimates by Qi et al. (2015) place the CO snow line at a midplane radius of 90 AU, corresponding to a gas and dust temperature of ~ 24 K in this disk. Recent work has revealed that the disk consists of several rings and gaps in the millimeter dust and in the gas (Isella et al. 2016), while the CO gas shows asymmetries at specific velocities (Pinte et al. 2018; Teague et al. 2018), both of which may be indicative of planet-disk interaction from embedded forming planets. Given its large radial extent of ~ 550 AU and resolved, relatively close-in CO snow line position, HD 163296 is one of the best candidates to probe the formation of

organics that require the freeze-out of abundant volatiles such as CO.

This paper presents observations from the Atacama Large Millimeter/submillimeter Array (ALMA) of the CH_3OH molecule toward HD 163296. Section 2 describes the observations and data reduction. Results including the upper limits on the methanol content of the HD 163296 disk and a comparison to the TW Hya disk are described in Section 3. In Section 4 we discuss the implications of the upper limits on the detectability of methanol in disks similar to HD 163296. Section 5 presents the conclusions of this work.

2. Observations and reduction

HD 163296 (J2000: R.A. = $17^{\text{h}}56^{\text{m}}21.280^{\text{s}}$, DEC = $-21^\circ57'22.441''$) was observed with ALMA in band 6 and band 7 during Cycle 4 under project 2016.1.00884.S. Band 6 and band 7 are receivers operating in the 211–275 GHz and 275–373 GHz range, respectively. Band 6 observations were done with the ALMA 12-meter array on 2016 November 11, 2016 December 01, and 2017 March 15 with 42 antennas. Band 7 observations were carried out with the Atacama Compact Array (ACA) on 2016 October 05, 08, 13, 26 using 10 of the 7-meter ACA antennas, and with the ALMA 12-meter array on 2017 April 13 using 45 antennas. In total, four transitions of CH_3OH were targeted across the two bands with the frequency domain mode (FDM) correlator setting: two CH_3OH $5_{05}-4_{04}$ (A/E) lines² in band 6 at 241.791 GHz and 241.700 GHz with a frequency (velocity) resolution of 244 kHz (0.303 km s^{-1}); and in band 7, CH_3OH $2_{11}-2_{02}$ (A) at 304.208 GHz and CH_3OH $1_{10}-1_{01}$ (A) at 303.367 GHz with a frequency (velocity) resolution of 141 kHz (0.139 km s^{-1}). All CH_3OH lines were in the upper side band (USB) of their execution blocks. The lower side band (LSB) contained observations of the continuum, C^{17}O $J = 2 - 1$, CN $J = 2 - 1$, and CH_3CN $J = 13 - 12$ in band 6, and the continuum, DCN $J = 4 - 3$, and four H_2CO lines in band 7 which will be presented in Guzmán, et al. (in prep). Table 1 summarizes the observational parameters for each CH_3OH line and the continuum.

Band 6 observations were obtained over three execution blocks with 6.05 sec integration steps and 68 minutes total time on-source. System temperatures varied from 60–140 K and the average precipitable water vapor varied from 1.5–2.3 mm. J1924-2914 was the bandpass calibrator and Titan was the flux calibrator for all execution blocks. The average flux values for Titan were: 1.15 Jy in the USB and 1.01 Jy in the LSB for 2016 November 11 and December 01; 0.963 Jy in the USB and 0.846 Jy in the LSB for 2017 March 15. The gain calibrator was different for each execution block: J1745-2900 on 2016 November 11, J1742-1517 on 2016 December 01, and J1733-1304 on 2017 March 15. The derived flux values for J1745-2900, J1742-1517, and J1733-1304 were 3.29 Jy, 0.212 Jy, and 1.47 Jy, respectively. All measurement sets were subsequently concatenated and time binned to 30s integration time per visibility for imaging and analysis.

Band 7 observations were obtained with the 12-meter array over three execution blocks with 6.05 sec integration steps and 105 minutes total time on-source. Data was also obtained with the ACA over four execution blocks with 10.1 sec integration

¹ The updated distance $d = 101 \pm 1$ pc results in a stellar luminosity of $\sim 23 L_\odot$, which is 30% lower than the previous estimate (Alecian et al. 2013). Applying the adjusted luminosity value to the H-R diagram used by Alecian et al. (2013) to determine the age of the system and stellar mass results in an updated age of ~ 9 Myr and an adjusted stellar mass closer to $2.1 M_\odot$.

² As a methyl group molecule, methanol exists in three forms with different hydrogen spin symmetry properties. The A-type form has a total spin 3/2, while the E-type form is degenerate having E^a and E^b varieties with total spin 1/2. The ratio of A-type to E-type forms of methanol is one.

Table 1: HD 163296 observational parameters

Band 6		
Dates Observed	2016 November 11, December 01; 2017 March 15	
Baselines	15 – 1000 m 12 – 776 kλ	
	CH ₃ OH 5 ₀₅ –4 ₀₄ (E)	CH ₃ OH 5 ₀₅ –4 ₀₄ (A)
Rest frequency [GHz]	241.700	241.791
Synthesized beam [FWHM]	1.46'' × 1.13''	1.46'' × 1.13''
Position angle	–76.6°	–76.6°
Channel width [km s ^{–1}]	0.303	0.303
rms noise ^a [mJy beam ^{–1}]	3.0	3.0
Weighting	natural	natural
Continuum frequency [GHz]	233.0	
Synthesized beam [FWHM]	0.55'' × 0.37''	
Position angle	76.8°	
rms noise [mJy beam ^{–1}]	0.17	
Integrated flux [mJy]	754 ± 75	
Weighting	Briggs, robust = 0.5	
Band 7		
Dates Observed	ACA	2016 October 05, 08, 13, 26
	12-meter array	2017 April 13
Baselines	ACA	9 – 49 m 9 – 48 kλ
	12-meter array	15 – 460 m 15 – 454 kλ
	CH ₃ OH 1 ₁₀ –1 ₀₁ (A)	CH ₃ OH 2 ₁₁ –2 ₀₂ (A)
Rest frequency [GHz]	303.367	304.208
Synthesized beam [FWHM]	1.37'' × 1.14''	1.36'' × 1.15''
Position angle	91.1°	90.6°
Channel width [km s ^{–1}]	0.139	0.139
rms noise ^a [mJy beam ^{–1}]	2.5	2.5
Weighting	natural	natural
Continuum frequency [GHz]	296.0	
Synthesized beam [FWHM]	0.63'' × 0.48''	
Position angle	87.8°	
rms noise [mJy beam ^{–1}]	0.09	
Integrated flux [mJy]	1288 ± 128	
Weighting	Briggs, robust = 0.5	

Notes. Flux calibration accuracy is taken to be 10%. For specifics on the line transition data, see Table 2. ^(a) Noise levels are per image channel.

steps and 184 minutes total time on-source. System temperatures varied from 80–150 K and the average precipitable water vapor varied from 0.5–1.1 mm. J1924–2914 was the bandpass calibrator for all execution blocks. Titan, Neptune, J1733–1304, and J1751+0939 were used as flux calibrators. The average flux values were: Titan – 1.96 Jy in the USB and 1.82 Jy in the LSB for 2017 April 13; Neptune – 22.5 Jy in the USB and 21.2 Jy in the LSB for 2016 October 08, 26; J1733–1304 – 1.32 Jy (2017 April 13), 1.14 Jy (2016 October 13) in the USB and 1.36 Jy (2017 April 13), 1.18 Jy (2016 October 13) in the LSB; J1751+0939 – 1.58 Jy in the USB and 1.60 Jy in the LSB for 2016 October 05. The gain calibrators were J1733–1304 for the 12-meter array data and J1745–2900 for the ACA data. The derived flux value for J1733–1304 was 1.36 Jy (2017 April 13) and the values for J1745–2900 were 3.2 Jy (2016 October 05, 08, 13), and 4.6 Jy (2016 October 26). All measurement sets were subsequently concatenated and time binned to 30 sec integration time per visibility for imaging and analysis.

Self-calibration for HD 163296 in band 6 was done with five spectral windows dedicated to continuum observations: two in the LSB at 223.5 GHz and 224 GHz and three in the USB at 234

GHz, 241 GHz, and 242 GHz with a total combined bandwidth of 469 MHz. The band 6 reference antenna was DA41. Band 7 self-calibration was done with three spectral windows dedicated to continuum observations: one in the LSB at 289 GHz and two in the USB at 302 GHz and 303.5 GHz with a total combined bandwidth of 469 MHz. The band 7 reference antenna was DA59 for the 12-meter array and CM03 for the ACA. A minimum of four baselines per antenna and a minimum signal-to-noise ratio (SNR) of two were required for self-calibration. Calibration solutions were calculated twice for phase and once for amplitude. The first phase solution interval (solint) was 200 sec, the second phase and amplitude solutions had solint equal to the binned integration time (30 sec). Self-calibration solutions for the continuum spectral windows were mapped to the line spectral windows nearest in frequency. Continuum subtraction for the line data was done in the *uv* plane using a single-order polynomial fit to the line-free channels. CLEAN imaging was performed with natural weighting for each continuum-subtracted CH₃OH line with a *uv* taper to achieve a 1'' beam in order to increase the sensitivity.

This paper also makes use of Submillimeter Array (SMA) H₂CO data for the HD 163296 disk (Qi et al. 2013), ALMA

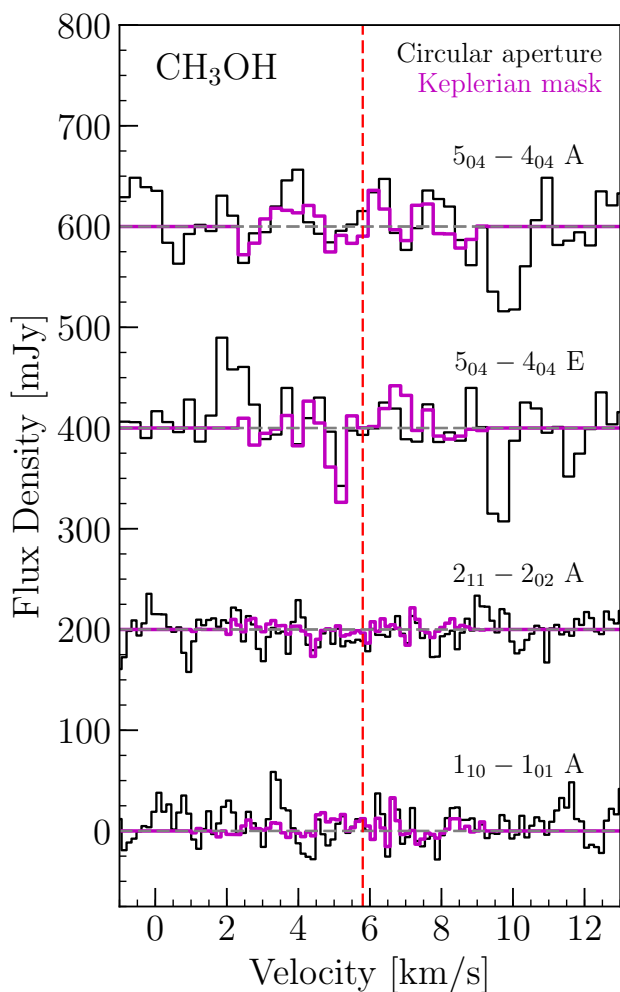


Fig. 1: Spectra at the expected velocity of CH₃OH line emission in the HD 163296 disk showing non-detections from aperture-masked image cubes using an 8'' diameter circular aperture (black) and Keplerian-masked image cubes (magenta). The two bottom spectra are observed in band 7 in 0.139 km s⁻¹ channels while the two top spectra are in band 6 in 0.303 km s⁻¹ channels. The horizontal gray dashed line represents the spectrum baseline, which is offset by 200 mJy for each line. The vertical red dashed line shows the systemic velocity at 5.8 km s⁻¹ (Qi et al. 2011).

H₂CO data for the HD 163296 disk (Carney et al. 2017), ALMA H₂CO data for the TW Hya disk (Öberg et al. 2017), and ALMA CH₃OH data for the TW Hya disk (Walsh et al. 2016). The following software and coding languages are used for data analysis: the CASA package version 4.7.2 (McMullin et al. 2007) and PYTHON.

3. Results

No methanol lines listed in Table 1 are detected in the disk around HD 163296 neither individually nor after line stacking. In this section, we first describe the stacking and masking methods used to maximize the SNR to attempt to extract the disk-integrated intensity of the CH₃OH lines. The method used to estimate the column density and abundance of methanol in the HD 163296 disk is then described. A comparison is presented between the CH₃OH and H₂CO content in the disks around HD

163296 and TW Hya based on data taken from the literature. Finally, model spectra of the band 7 CH₃OH lines are created for HD 163296 and compared to the sensitivity of the observations.

3.1. Line extraction

We attempt to extract the targeted CH₃OH lines from the CLEANed image cubes using a circular aperture with an 8'' diameter centered on the source, which yields no detections (see Figure 1). To increase the SNR we repeat this analysis after stacking the CH₃OH lines using different line stacking schemes. We further attempt to increase the SNR of the CH₃OH data by applying masking techniques: Keplerian masking in the image plane, and matched filter analysis in the *uv* plane to search for any signal in the raw visibilities.

3.1.1. Line stacking

Stacking is done for band 6 and band 7 lines separately, and then again for both bands together. The band 7 lines are more easily excited due to their lower upper energy ($E_u < 22$ K) values compared to the band 6 lines ($E_u > 34$ K; see Table 2), thus band 7 observations should be sensitive to lower CH₃OH column densities and should be easier to detect. Note that the level populations are likely to be in LTE for the expected methanol emitting region where gas densities in the disk are high ($\gtrsim 10^7$ cm⁻³), thus we do not expect the critical density of the lines to influence the amount of line emission (see Table 2).

First, we stack the lines in the image plane by adding together the integrated intensity maps ($v = 2.4 - 9.2$ km s⁻¹) created from the CH₃OH continuum-subtracted and *uv*-tapered CLEANed image cubes. Second, we stack in the *uv* plane by concatenating ALMA measurement sets prior to imaging. Stacking in the *uv* plane is done using the CASA `cvel` function, which is used to regrid the velocity axis of line data and has the option to combine visibility data for multiple lines. For *uv* stacking across all bands, the band 7 lines are regridded to 0.303 km s⁻¹ channels to match the channel width of the band 6 lines. Methanol remains undetected after implementing the stacking methods described above.

3.1.2. Keplerian masking in the image plane

For maximum SNR in the image plane, we apply a Keplerian mask to the CLEANed image cube for each CH₃OH line (Carney et al. 2017; Salinas et al. 2017) to exclude noisy pixels that are not associated with the emission expected from a disk in Keplerian rotation. The mask is based on the velocity profile of a rotating disk, which is assumed to be Keplerian around a central stellar mass of $M = 2.3 M_\odot$ (Alecian et al. 2013). A subset of pixels (x, y, v) are identified in the CH₃OH image cubes where the Doppler-shifted line velocity projected along the line of sight matches the pixel Keplerian velocity (x, y, v_K) projected along the line of sight. Pixels with velocities that do not match the Keplerian rotational profile criteria are masked. Integrated intensity maps and disk-integrated spectra are again created from the Keplerian-masked cubes of the CH₃OH lines individually and after line stacking; however, in all cases, CH₃OH remains undetected. Figure 1 shows the aperture-masked spectra and the Keplerian-masked spectra of the four methanol lines targeted in HD 163296.

Upper limits on the integrated intensity for each CH₃OH line are calculated using the projected Keplerian mask (x, y, v_K) de-

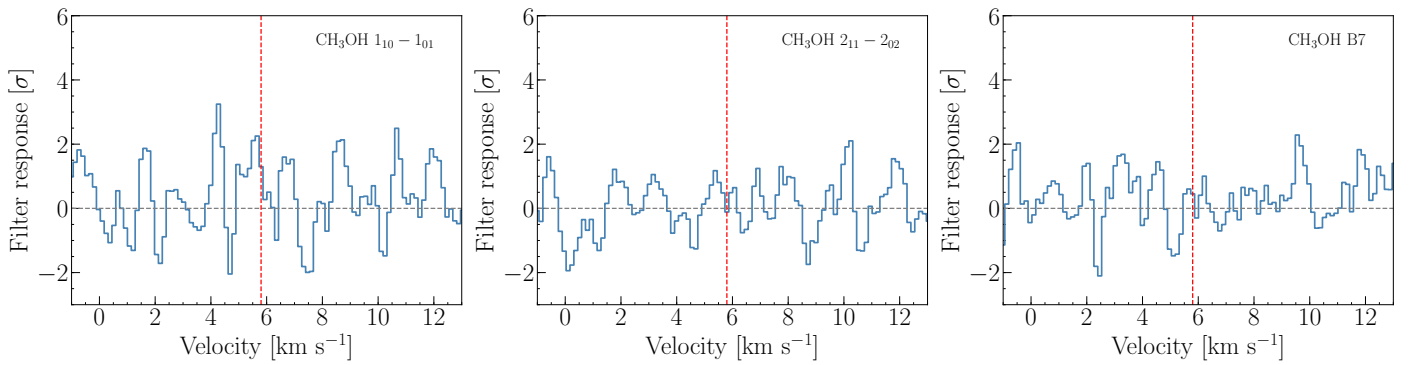


Fig. 2: Matched filter results for the band 7 CH₃OH lines in the HD 163296 disk using the H₂CO emission as a template. A peak $> 3\sigma$ at the source velocity ($v = 5.8 \text{ km s}^{-1}$; red dashed line) would signify a positive detection of methanol. The band 7 lines should be the strongest in our sample, but there is no evidence of CH₃OH in the matched filter for the band 7 individual lines nor the band 7 stacked lines. (Left) CH₃OH $1_{10}-1_{01}$ (A) line. (Middle) CH₃OH $2_{11}-2_{02}$ (A) line. (Right) Stacked band 7 CH₃OH lines.

rived for the HD 163296 disk. To obtain the strictest upper limits on the integrated line intensity, we include only the positions and velocities associated with the disk. Therefore, the mask cube contains pixels set equal to unity for (x, y, v_K) positions only, and all other pixels are set to zero. The upper limit is set at 3σ where $\sigma = \delta v \sqrt{N} \sigma_{\text{rms}}$, δv is the velocity channel width in km s^{-1} , N is the number of independent measurements contained within the projected Keplerian mask, and σ_{rms} is the rms noise per channel in mJy beam^{-1} (see Table 1). To account for correlated noise within the size of the beam, we sum over all (x, y, v_K) pixel positions and divide by the number of pixels per beam n_{ppb} , to get $N = \Sigma(x, y, v_K) / n_{\text{ppb}}$, the number of independent measurements over the integrated Keplerian mask. The disk-integrated upper limits for each CH₃OH line are listed in Table 2.

3.1.3. Matched filter analysis in the uv plane

To maximize the SNR in the uv plane, we apply a matched filter to the CH₃OH line visibility data (Loomis et al. 2018). In this technique, a template image cube is sampled in uv space to obtain a set of template visibilities that act as the filter. The filter is then cross-correlated with a set of low SNR visibilities (in this case, the CH₃OH data) in an attempt to detect any signal that is co-spatial with the template emission. Loomis et al. (2018) and Carney et al. (2017) have published positive detections using the matched filter technique for CH₃OH and H₂CO, which can provide an improvement in SNR of $>50\text{--}500\%$ over the traditional aperture masking, depending on the spectral resolution of the observed visibilities.

We use the H₂CO $3_{03}-2_{02}$ detection towards the HD 163296 disk reported in Carney et al. (2017) as the template emission profile under the assumption that CH₃OH and H₂CO reside in similar regions. The emission morphologies will be dominated primarily by Keplerian rotation, therefore a high degree of co-spatiality is expected. The H₂CO line is re-imaged with CLEAN to achieve a spatial and spectral resolution equal to the observed CH₃OH lines. Channels with H₂CO emission ($v = 1.6 - 10 \text{ km s}^{-1}$) are sampled in uv space using the PYTHON `vis_sample`³ routine. The matched filter is run for the CH₃OH line visibility data individually and after line stacking.

Figure 2 shows the spectrum that is produced by the matched filter analysis for the band 7 CH₃OH data. The filter response in units of σ is the measure of the SNR of the cross-correlation between the CH₃OH line visibility data and the filter derived from the template H₂CO emission. A correlation between the CH₃OH data and the filter would result in a peak at the source velocity. No such feature is seen in the filter response spectrum of any CH₃OH lines in the HD 163296 disk, suggesting that the detection threshold for methanol is well below the sensitivity achieved in our ALMA observations. The matched filter analyses confirm the non-detection of CH₃OH found during analysis in the image plane. The same analysis for the band 6 lines also results in no detection, which is expected given that the band 7 lines should be brighter.

3.2. CH₃OH column density and abundance upper limits

We estimate the disk-averaged column density of CH₃OH based on the integrated line intensity upper limit, an assumed excitation temperature, and the total disk mass. Following the formula used by Remijan et al. (2003) and Miao et al. (1995) for optically thin emission in local thermodynamic equilibrium (LTE), we can estimate the column density

$$N = 2.04 \frac{\int I_\nu dv}{\theta_a \theta_b} \frac{Q_{\text{rot}} \exp(E_u/T_{\text{ex}})}{v^3 \langle S_{\text{ul}} \mu^2 \rangle} \times 10^{20} \text{ cm}^{-2}, \quad (1)$$

where $\int I_\nu dv$ is the integrated line intensity in $\text{Jy beam}^{-1} \text{ km s}^{-1}$, θ_a and θ_b correspond to the semi-major and semi-minor axes of the synthesized beam in arcseconds, T_{ex} is the excitation temperature in K, and ν is the rest frequency of the transition in GHz. The partition function (Q_{rot}), upper energy level (E_u , in K), and the temperature-independent transition strength and dipole moment ($S_{\text{ul}} \mu^2$, in debye^2) for CH₃OH are taken from the Cologne Database for Molecular Spectroscopy (CDMS; Müller et al. 2005).

Methanol is expected to form primarily in ice in cold regions of protoplanetary disks, where gas densities are higher ($\sim 10^9 \text{ cm}^{-3}$; Walsh et al. 2014) than the critical density of the observed CH₃OH transitions ($10^6 - 10^7 \text{ cm}^{-3}$; Rabli & Flower 2010). Recent physical models of the HD 163296 disk have gas densities $> 10^6 \text{ cm}^{-3}$ in the region $z/r < 0.4$ (Qi et al. 2011; de Gregorio-Monsalvo et al. 2013; Rosenfeld et al. 2013), where z

³ `vis_sample` is publicly available at https://github.com/AstroChem/vis_sample or in the Anaconda Cloud at https://anaconda.org/rloomis/vis_sample

Table 2: Disk-averaged column density and abundance of CH₃OH in HD 163296 and TW Hya.

Object	Line	$\int I_\nu dv^\dagger$ [mJy km s ⁻¹]	E_u [K]	$\log(A_{ul})$ [s ⁻¹]	n_{crit}^a [cm ⁻³]	N_{avg} [cm ⁻²]	CH ₃ OH/H ₂
HD 163296	CH ₃ OH 5 ₀₅ –4 ₀₄ (E)	< 51	47.9	–4.22	1.6(06)	< 6.9(12)	< 2.1(–11)
	CH ₃ OH 5 ₀₅ –4 ₀₄ (A)	< 51	34.8	–4.22	4.3(05)	< 4.1(12)	< 1.3(–11)
	CH ₃ OH 1 ₁₀ –1 ₀₁ (A)	< 26	16.9	–3.49	4.3(07)	< 7.0(11)	< 2.2(–12)
	CH ₃ OH 2 ₁₁ –2 ₀₂ (A)	< 26	21.6	–3.49	5.0(06)	< 5.0(11)	< 1.6(–12)
TW Hya	CH ₃ OH stacked [*]	26.5 ± 2.7 ^c	28.6	–3.49	3.0(06)	4.7(12)	1.1(–12)

Notes. The disk-averaged column density is calculated using Equation 1 with $T_{ex} = 25$ K. The format $a(b)$ translates to $a \times 10^b$. Flux errors are dominated by systematic uncertainties, taken to be 10%.

^(†) Upper limits are derived at the 3σ level using the HD 163296 Keplerian mask (see Section 3).

^(*) The stacked detection consists of three CH₃OH transitions: CH₃OH 2₁₁–2₀₂ (A) at 304.208 GHz, CH₃OH 3₁₂–3₀₃ (A) at 305.472 GHz, and CH₃OH 4₁₃–4₀₄ (A) at 307.166 GHz. Excitation parameters for the CH₃OH 3₁₂–3₀₃ (A) line are used to calculate column density.

References: ^(a) Rabli & Flower (2010); ^(b) Walsh et al. (2016).

and r are the disk height and radius, respectively. In recent models of the TW Hya disk, Walsh et al. (2016) varied the methanol emitting region over the range $z/r < 0.1$, $0.1 < z/r < 0.2$, and $0.2 < z/r < 0.3$, which all fit the data equally well. These models all had methanol present at $z/r < 0.3$, suggesting that emission is arising from dense regions within the disk. Under these conditions, LTE is a reasonable assumption, and thus T_{ex} is expected to equal the kinetic temperature of the gas.

Assuming optically thin emission, the disk-averaged column density can be used to estimate the total number of CH₃OH molecules in the disk $N(\text{CH}_3\text{OH}) = N_{avg}(a \times b)$, where $(a \times b)$ is the total emitting area of the disk. Assuming the total disk mass is primarily molecular hydrogen, we can estimate the total number of H₂ molecules $N(\text{H}_2) = M_{disk}/m_{\text{H}_2}$, where m_{H_2} is the molecular hydrogen mass. The CH₃OH emitting area is set to $a = b = 7''$ based on the H₂CO emission diameter in the HD 163296 disk (Carney et al. 2017), assuming a similar chemical origin and distribution. The total disk mass is $\sim 0.09 M_\odot$ based on models of CO observations (Qi et al. 2011; Rosenfeld et al. 2013). Table 2 shows the disk-averaged column density and abundance for the single temperature assumption $T_{ex} = 25$ K in LTE, which is approximately the same as the excitation temperature found for H₂CO in the HD 163296 disk (Qi et al. 2013; Carney et al. 2017). The CH₃OH 2₁₁–2₀₂ (A) line provides the strictest upper limit on the methanol column density and abundance in HD 163296, with $N_{avg} \lesssim 5.0 \times 10^{11} \text{ cm}^{-2}$ and $\text{CH}_3\text{OH}/\text{H}_2 \lesssim 1.6 \times 10^{-12}$, based on its disk-integrated line intensity upper limit and assuming an excitation temperature of $T_{ex} = 25$ K. Table A.1 in the Appendix shows the disk-averaged column density and abundance for a range of LTE excitation conditions with $T_{ex} = 25, 50$, and 75 K. The abundances do not vary with T_{ex} by more than a factor of 2–3 in the most extreme cases.

3.3. H₂CO and CH₃OH in HD 163296 and TW Hya

We estimate the fraction of methanol relative to formaldehyde based on our upper limits for CH₃OH in HD 163296 and compare to the TW Hya disk, the only Class II protoplanetary disk for which there is a gas-phase methanol detection (Walsh et al. 2016). Integrated line intensities for H₂CO detections in HD

163296 and TW Hya are taken from the literature, and their disk-averaged column densities and abundances are derived in the same manner as described in Section 3.2 to ensure consistency when comparing the H₂CO and CH₃OH content. The TW Hya disk mass is $0.05 M_\odot$ based on observations of the HD molecule (Bergin et al. 2013). The emitting area for H₂CO in TW Hya is set to $a = b = 3''$ based on the diameter of emission observed by Öberg et al. (2017). The same $3''$ emitting area is used for CH₃OH in TW Hya. Table 3 shows the calculated column densities and abundances for the H₂CO observations.

For HD 163296, the CH₃OH 2₁₁–2₀₂ (A) line is used to calculate the methanol-to-formaldehyde ratio as it gives the strictest upper limits on the methanol abundance. For TW Hya, we obtained the integrated line intensity of the stacked methanol detection by Walsh et al. (2016), assume that the majority of emission is due to the strongest individual line (CH₃OH 3₁₂–3₀₃ (A) at 305.473 GHz with $E_u = 28.6$ K: Walsh et al. 2014; Loomis et al. 2018), and use the excitation parameters of that line with Equation 1 to derive the TW Hya CH₃OH column density and abundance, and subsequently the CH₃OH/H₂CO ratio for the disk.

Results for the CH₃OH/H₂CO ratio in TW Hya and HD 163296 can be found in Table 3. Ratios calculated with the H₂CO 3₁₂–2₁₁ line should be representative of the true CH₃OH/H₂CO ratio since the H₂CO 3₁₂–2₁₁ upper energy level (E_u), Einstein A coefficient (A_{ul}), and critical density (n_{crit}) are similar to that of the band 7 methanol lines observed in these disks. Thus, we obtain CH₃OH/H₂CO ratios of < 0.24 for HD 163296 and 1.27 for TW Hya, which suggests that the disk around HD 163296 is less abundant in methanol relative to formaldehyde compared to the TW Hya disk.

3.4. Model CH₃OH spectra for HD 163296

In addition to the extraction methods described in previous sections, we also attempt a forward modeling approach to interpret the CH₃OH non-detections toward HD 163296. We model the HD 163296 CH₃OH band 7 spectra using a parameterized disk structure and radiative transfer methods in order to compare the modeled emission to the noise level in the Keplerian-masked image cubes. We adopt the physical structure and the abundance

Table 3: Disk-averaged column density and abundance of H₂CO in HD 163296 and TW Hya.

Object	Line	$\int I_\nu d\nu$ [mJy km s ⁻¹]	E_u [K]	$\log(A_{ul})$ [s ⁻¹]	n_{crit}^a [cm ⁻³]	N_{avg} [cm ⁻²]	H ₂ CO/H ₂	CH ₃ OH/H ₂ CO [†]
HD 163296	H ₂ CO 3 ₁₂ –2 ₁₁	890 ± 89 ^b	33.4	–3.55	5.7(06)	2.1(12)	6.3(–12)	< 0.24
TW Hya	H ₂ CO 3 ₁₂ –2 ₁₁	291 ± 29 ^c	33.4	–3.55	5.7(06)	3.7(12)	8.9(–13)	1.27 ± 0.13

Notes. The disk-averaged column density is calculated using Equation 1 with $T_{\text{ex}} = 25$ K. The format $a(b)$ translates to $a \times 10^b$. Flux errors are dominated by systematic uncertainties, taken to be 10%.

^(†) Ratios are determined using the CH₃OH disk-integrated column density from Table 2. HD 163296: based on the strictest upper limit from the CH₃OH 2₁₁–2₀₂ (A) line. TW Hya: based on the stacked CH₃OH detection.

References: ^(a) Wiesenfeld & Faure (2013); ^(b) Qi et al. (2013); ^(c) Öberg et al. (2017).

structure of the model used by Carney et al. (2017) to reproduce ALMA observations of H₂CO in the HD 163296 disk, then scale the CH₃OH abundance with respect to the H₂CO abundance. The Line Modeling Engine (LIME; Brinch & Hogerheijde 2010) 3D radiative transfer code is run in LTE with 10000 grid points at the source distance of the original Qi et al. (2011) physical model ($d = 122$ pc) to create synthetic images of the CH₃OH observations. The synthetic images are continuum-subtracted, sampled in uv space with the PYTHON `vis_sample` routine, and imaged with CLEAN at the same velocity resolution as the observations.

Figure 3 shows the disk-integrated model spectra for the CH₃OH band 7 lines for a range of methanol-to-formaldehyde ratios, as indicated by the legend. The spectra show that a line should have been detected in the disk around HD 163296 for a CH₃OH/H₂CO ratio of ~ 0.2 for the most sensitive case (stacked band 7 lines). This result is consistent with the upper limit on this ratio derived from the integrated intensity of the Keplerian mask cube as presented in Section 3.3.

4. Discussion

The results presented in Table 3 suggest that the HD 163296 disk has a lower overall gas-phase methanol content with respect to formaldehyde than the TW Hya disk. In this section we discuss possible reasons for a lower CH₃OH/H₂CO ratio in HD 163296, as well as a brief assessment of the observing time needed to detect the low predicted abundances of gas-phase methanol in this disk.

4.1. The CH₃OH/H₂CO ratio in HD 163296 and TW Hya

It should be noted that there are uncertainties on the order of a factor of a few when deriving the CH₃OH/H₂CO ratio as described in this work. Namely, the column density calculation for the methanol detection in TW Hya is a result of three stacked line transitions rather than a single common transition as for H₂CO observed in both disks. The CH₃OH 3₁₂–3₀₃ (A) line at 305.473 GHz is the strongest methanol line observed in TW Hya, but it is not the sole contributor to the detected line emission. However, even if all three lines are equally strong and the 305.473 GHz line contributes only 33% to the total stacked line intensity, then the inferred TW Hya CH₃OH/H₂CO ratio of 0.42 is still higher than our upper limit for HD 163296 of < 0.24. Matched filter analysis of the TW Hya CH₃OH detections (e.g., Figure 7 in Loomis et al. 2018) shows that the CH₃OH 3₁₂–3₀₃ (A) line is indeed stronger than the other two band 7 lines used by Walsh

et al. (2016) for line stacking, suggesting that a contribution of $\sim 50\%$ to the stacked emission is a reasonable estimate.

Modeling by Willacy (2007) explored complex gas-grain chemical models of protoplanetary disks including H₂CO and CH₃OH with the following desorption processes: thermal desorption, desorption due to cosmic-ray heating of grains, and photodesorption. Their models, based on the UMIST Database for Astrochemistry network, show that outer disk abundances should give CH₃OH/H₂CO ≈ 0.04 , which is lower than both the ratio found for TW Hya and the upper limit on the ratio found for HD 163296. However, these models neglected radical-radical pathways to form larger complex organic molecules. Gas-grain chemical models by Semenov & Wiebe (2011) based on the Ohio State University (OSU) network predict low column densities of methanol ice due to the high diffusion barrier used in the grain-surface chemistry, which highlights the importance of the assumed chemical parameters in these models. Their models and work by Furuya & Aikawa (2014) show that production of CH₃OH is sensitive to turbulent mixing and that the abundance of gas-phase CH₃OH, and thus the CH₃OH/H₂CO ratio, will increase when turbulent mixing is strong. The HD 163296 disk has a low degree of turbulence $\lesssim 0.05 c_s$ (Flaherty et al. 2015, 2017), while the TW Hya disk has similar low values of $\lesssim 0.05$ – $0.10 c_s$ (Flaherty et al. 2018), suggesting vertical mixing is not strong in these disks.

Other recent work by Walsh et al. (2014) based on the OSU network investigates the production of complex molecules in disks, including H₂CO and CH₃OH, using an extensive full chemical network with chemical ingredients similar to the previously mentioned works. Their models include two-body, X-ray, and cosmic ray reactions and photoreactions in the gas phase and on grain surfaces as all as gas-grain reactions (e.g., freeze-out and photodesorption) around a T Tauri-like PMS star. The models in that work show that their outer disk ($R = 250$ AU) hosts a large methanol and formaldehyde ice reservoir with a sufficient number of these molecules released into the gas phase to give CH₃OH/H₂CO ≈ 0.33 . Subsequent work by Walsh et al. (2015) examines molecular complexity across different luminosities (M dwarf, T Tauri, Herbig Ae/Be) for the inner disk following a similar modeling approach. The authors find that molecular organics like H₂CO and CH₃OH contribute to the disk gas-phase carbon and oxygen reservoir for the cooler PMS stars, but not for the warmer Herbig Ae/Be PMS stars. These modeling results perhaps point to important differences in how these two molecules are formed in T Tauri disks versus Herbig Ae/Be disks.

The underlying physical structure in the TW Hya disk and the HD 163296 disk might explain the observed discrepancy be-

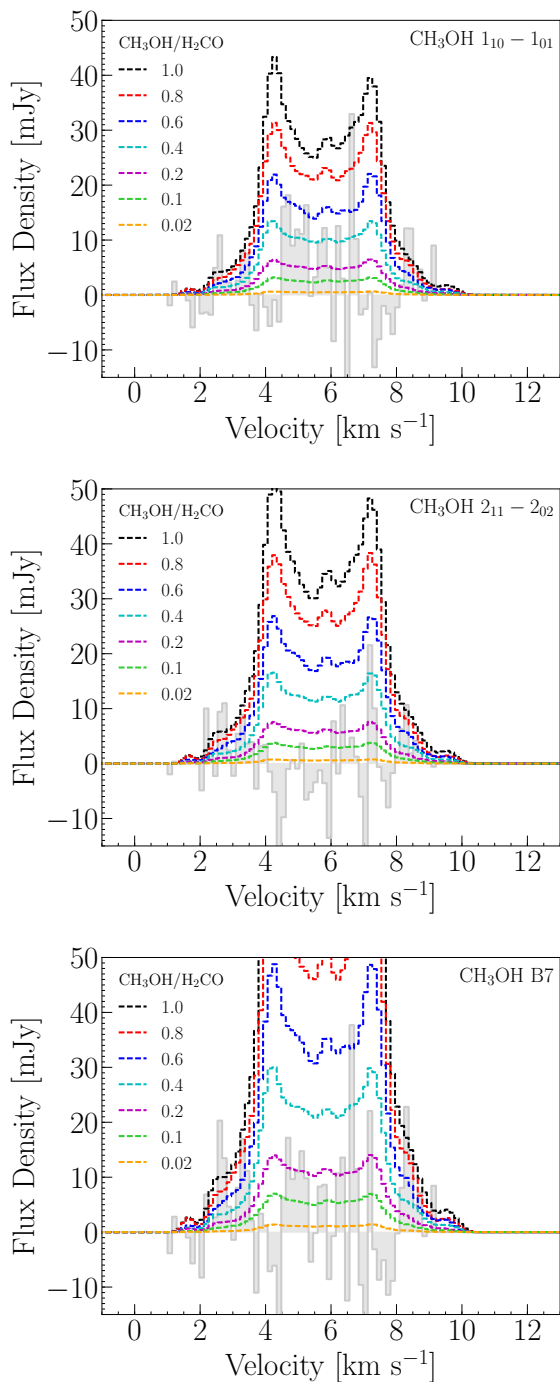


Fig. 3: Model CH_3OH spectra at different $\text{CH}_3\text{OH}/\text{H}_2\text{CO}$ abundance ratios (colored spectra lines) compared to the ALMA CH_3OH non-detections after Keplerian masking (gray) in the HD 163296 disk. Given the sensitivity levels achieved, the ALMA observations should be sensitive to the presence of methanol in the disk for $\text{CH}_3\text{OH}/\text{H}_2\text{CO} \gtrsim 0.2$ based on the stacked band 7 lines. (Top) $\text{CH}_3\text{OH } 1_{10}-1_{01}$ (A) line. (Middle) $\text{CH}_3\text{OH } 2_{11}-2_{02}$ (A) line. (Bottom) Stacked band 7 CH_3OH lines.

tween their $\text{CH}_3\text{OH}/\text{H}_2\text{CO}$ ratios. Recent observations of sub-millimeter and scattered light in these disks highlight important differences in their dust structure. The micron-sized dust observed in scattered light is highly coupled to the gas and traces the surface layers of the disk, while millimeter-sized

dust has mostly decoupled from the gas and settled toward the disk midplane (Dullemond & Dominik 2004; D’Alessio et al. 2006; Williams & Cieza 2011). The TW Hya disk was observed with ALMA in the band 6 continuum at $850 \mu\text{m}$ and with VLT/SPHERE in H -band at $1.62 \mu\text{m}$ (Andrews et al. 2016; van Boekel et al. 2017), showing several rings and gaps in both millimeter- and micron-sized dust. The micron-sized dust rings tracing the surface layers extend beyond the millimeter-sized dust in this disk. In contrast, recent scattered light observations by VLT/SPHERE in H -band, Keck/NIRC2 in J -band, and ALMA 1.3 millimeter observations of the HD 163296 disk show that no scattered light is observed beyond the innermost millimeter dust ring, suggesting that the surface layers of the outer disk are relatively flat and may be shadowed by the innermost dust ring (Muro-Arena et al. 2018; Guidi et al. 2018). Ultraviolet radiation from the central star can release molecular ices back into the gas phase via UV photodesorption (Öberg et al. 2009, 2015; Huang et al. 2016), which may be suppressed if the HD 163296 outer disk is shadowed.

Alternatively, both disks may have a similar degree of UV irradiation, but as a Herbig Ae star HD 163296 will have a harder UV spectrum than TW Hya, which is dominated by Lyman- α emission (e.g., Figure 1 in Walsh et al. 2015). The UV photodesorption rate of methanol ice is a strong function of photon energy and absorption cross section (Cruz-Díaz et al. 2016), and therefore will depend on the shape of the radiation field as well as the strength (Bertin et al. 2016). A harder, stronger Herbig Ae radiation field will lead to more CH_3OH fragmentation upon photodesorption and thus methanol ice will be converted into other gas-phase species which could go on to seed H_2CO formation in the gas phase.

Another possibility is that the HD 163296 disk formed from a protostar that did not inherit a large amount of methanol ice. Perhaps during formation, temperatures remained too warm for CO freeze-out needed to produce the high $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ice ratios seen in ISM ices. Chemical models with some methanol already formed at earlier stages (Walsh et al. 2014) host a more abundant methanol ice reservoir than models which start from atomic abundances, which have orders of magnitude lower methanol ice abundances (e.g., Molyarova et al. 2017).

While both formaldehyde and methanol are thought to be formed via hydrogenation of CO ices (Watanabe & Kouchi 2002), formaldehyde can also be formed in the gas phase. Recent chemical models by Agúndez et al. (2018) that do not include grain-surface chemistry are able to reproduce observed column densities of H_2CO , but not CH_3OH , in the outer regions of T Tauri and Herbig Ae/Be disks. Reactions between CH_3 and atomic oxygen can occur in the disk surface layers where oxygen-bearing species are photodissociated (Fockenberg & Preses 2002; Atkinson et al. 2006). This reaction, however, has not been shown to contribute significantly to the H_2CO abundance in recent chemical models of disks around T Tauri stars (Walsh et al. 2014). The contribution may be larger in warmer, strongly irradiated disks around Herbig Ae/Be stars. Ion-molecule chemistry – which has a large influence on the gas-phase reservoir in the intermediate layers of protoplanetary disks – involving e.g., HCO^+ , H_3O^+ , and H_3^+ may also contribute to the overall gas-phase H_2CO abundance (Vasyunin et al. 2008). It may be that the HD 163296 disk is particularly rich in H_2CO formed in the gas phase, thus reducing its overall $\text{CH}_3\text{OH}/\text{H}_2\text{CO}$ ratio. However, results from a recent analysis using the ortho-to-para ratio of H_2CO as a tool to investigate its chemical origins are consistent with significant grain-surface formation and subsequent desorption (Guzmán et al. 2018). Detailed chemical

models of the HD 163296 protoplanetary disk beyond the scope of this work are required to test and quantify the importance of the production and destruction routes for H₂CO and CH₃OH discussed here.

4.2. Detectability of methanol

We can estimate the required ALMA observing time for a 3σ detection of CH₃OH in the HD 163296 disk given a range of CH₃OH/H₂CO ratios consistent with our upper limit of < 0.24 . We consider methanol abundances relative to formaldehyde of 0.20, 0.10, 0.05, as these would be below our current 3σ upper limit of < 0.24 listed in Table 3. To observe the CH₃OH $2_{11}-2_{02}$ (A) line of methanol with similar spatial and spectral resolution at these assumed CH₃OH/H₂CO ratios, we would need to increase our sensitivity by factors of about ~ 1.5 , 2.5 , and 5 , respectively. Because the telescope sensitivity is inversely proportional to the square root of the observing time, $\sigma_S \propto 1/\sqrt{t}$, the time required to realize these increases in sensitivity would multiply by factors of 2.25 , 6.25 , and 25 , respectively. Based on the band 7 observations presented here with 105 minutes of total on-source time, these factors translate to total on-source times of ~ 4 hrs, ~ 11 hrs, ~ 44 hrs for methanol at 20%, 10%, and 5% of the formaldehyde content in HD 163296, respectively. The detection of 10% methanol relative to formaldehyde is a clear practical limit for the HD 163296 disk based on these required integration times.

Disk size has a significant effect on methanol detectability. Using our HD 163296 model, we decrease the outer radius of the disk and scale the disk physical structure (i.e., gas density and temperature) proportionally to test the effect of disk size on the band 7 methanol line strengths for Herbig disks similar to HD 163296. The LIME models are rerun for an outer disk radius from $R_{\text{out}} = 100 - 600$ AU in steps of 50 AU for CH₃OH/H₂CO = 0.10. The disk-integrated line intensity for the band 7 CH₃OH lines decreases by one order of magnitude for disks with $R_{\text{out}} = 250$ AU and by more than two orders of magnitude for disks with $R_{\text{out}} = 100$ AU. It is highly unlikely that methanol will be detected within an observing time of < 20 hours in most disks smaller than ~ 300 AU, considering the difficulty in detecting methanol relative to formaldehyde at the $< 25\%$ level in the HD 163296 disk, which has a radius of ~ 550 AU and a proximity closer than most nearby star-forming regions. These results depend on the assumption that CH₃OH shares the same extended emitting area as H₂CO.

It may be that the methanol lines targeted in this work are not suitable candidates for disks around Herbig Ae/Be stars. The choice to target these four CH₃OH lines with ALMA in band 6 and band 7 was motivated by the chemical modeling of a disk around a T Tauri star (Walsh et al. 2014) and by the methanol detection in the disk around TW Hya, also a T Tauri star (Walsh et al. 2016). Disks around Herbig Ae/Be stars are warmer, with a larger thermally desorbed inner reservoir due to the stronger stellar radiation. There is a potential reservoir of hot methanol in the inner disk atmosphere, similar to the hot water reservoir already observed in disks around less luminous T Tauri stars (Carr & Najita 2008; Salyk et al. 2008). Such emission could be compact yet still accessible in Herbig Ae/Be disks.

In summary, the CH₃OH lines in ALMA band 7 presented here should be detectable in disks with a CH₃OH/H₂CO ratio down to $\sim 10\%$ within realistic observing times, but only in disks with similar mass, size, distance, and H₂CO abundance as those found in the HD 163296 disk.

5. Conclusions

This paper presents ALMA observations targeting two CH₃OH lines in band 6 and two CH₃OH lines in band 7 in the protoplanetary disk around HD 163296. We determine upper limits on the abundance of methanol likely to be present in the HD 163296 disk and compare to TW Hya, currently the only Class II disk with a positive detection of gas-phase methanol. The conclusions of this work are as follows:

- None of the four CH₃OH lines are detected in the disk around HD 163296 individually nor after line stacking. Upper limits on the integrated intensity at the 3σ level are < 51 mJy km s⁻¹ for band 6 lines and < 26 mJy km s⁻¹ for band 7 lines. Neither aperture masking in the image plane, Keplarian masking in the image plane, nor matched filter analysis in the uv plane recover any methanol emission, indicating that our calculated 3σ upper limits are highly robust.
- The CH₃OH $2_{11}-2_{02}$ (A) line provides the strictest upper limit on the disk-averaged column density and abundance of methanol in the HD 163296 disk, with $N_{\text{avg}} < 5.0 \times 10^{11}$ cm⁻² and CH₃OH/H₂ $\lesssim 1.6 \times 10^{-12}$ at the 3σ level.
- The upper limit on the methanol-to-formaldehyde ratio in the HD 163296 disk is CH₃OH/H₂CO < 0.24 at the 3σ level. This ratio is lower than that of the TW Hya disk at CH₃OH/H₂CO = 1.27 ± 0.13 , indicating that the HD 163296 disk has a low amount methanol with respect to formaldehyde relative to the TW Hya disk.
- Possible explanations for the lower CH₃OH/H₂CO ratio in HD 163296 include: a low amount of gas-phase methanol is desorbed from icy grains at the disk midplane due to the flatter, shadowed disk geometry as seen in recent images taken by VLT/SPHERE; differences in the desorption processes in the HD 163296 disk compared to the TW Hya disk; and a higher-than-expected gas-phase formaldehyde abundance, as H₂CO may also be formed in the gas phase in the disk upper layers.
- To detect methanol at the 3σ level in the HD 163296 disk, we estimate that it is necessary to increase the total on-source observing time with the full ALMA 12-meter array up to 4 hours to be sensitive to CH₃OH/H₂CO $\approx 20\%$ and up to 11 hours to be sensitive to CH₃OH/H₂CO $\approx 10\%$. These estimates apply to other Herbig Ae/Be disks with masses, sizes, and distances similar to that found for the HD 163296 disk.

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Appendix A: Molecular abundances for different T_{ex}

Here the disk-averaged column densities and abundances are calculated for CH₃OH and H₂CO in the disk around HD 163296 and the disk around TW Hya for different excitation temperatures T_{ex} . The method used is described in Section 3.2. Equation 1 assumes optically thin emission and LTE excitation conditions. The excitation temperature T_{ex} is set to 25, 50 and 75 K, indicating different regions of the disk from which the emission lines may originate. At most, differences of factors 2–3 are seen in the disk-averaged column density and abundance for the values of T_{ex} explored here.

Table A.1: Disk-averaged column density and abundance of CH₃OH and H₂CO in HD 163296 and TW Hya for varying T_{ex} .

Object	Line	$\int I_\nu d\nu^\dagger$ [mJy km s ⁻¹]	E_u [K]	$\log(A_{ul})$ [s ⁻¹]	T_{ex} [K]	$n_{\text{crit}}^{a\ b}$ [cm ⁻³]	N_{avg} [cm ⁻²]	CH ₃ OH/H ₂	CH ₃ OH/H ₂ CO ^{††}
CH ₃ OH									
HD 163296	CH ₃ OH 5 ₀₅ –4 ₀₄ (E)	< 51	47.9	−4.22	25	1.6(06)	< 6.9(12)	< 2.1(−11)	
					50	1.9(06)	< 8.6(12)	< 2.6(−11)	
					75	2.1(06)	< 1.1(13)	< 3.5(−11)	
	CH ₃ OH 5 ₀₅ –4 ₀₄ (A)	< 51	34.8	−4.22	25	4.3(05)	< 4.1(12)	< 1.3(−11)	
					50	5.0(05)	< 6.6(12)	< 2.0(−11)	
					75	5.0(05)	< 9.6(13)	< 3.0(−11)	
	CH ₃ OH 1 ₁₀ –1 ₀₁ (A)	< 26	16.9	−3.49	25	4.3(07)	< 7.0(11)	< 2.2(−12)	
					50	5.6(07)	< 1.6(12)	< 5.0(−12)	
					75	6.4(07)	< 2.7(12)	< 8.2(−12)	
	CH ₃ OH 2 ₁₁ –2 ₀₂ (A)	< 26	21.6	−3.49	25	5.0(06)	< 5.0(11)	< 1.6(−12)	
					50	5.4(06)	< 1.1(12)	< 3.3(−12)	
					75	5.5(06)	< 1.7(12)	< 5.2(−12)	
TW Hya	CH ₃ OH stacked [*]	26.5 ± 2.7 ^c	28.6	−3.49	25	3.0(06)	4.7(12)	1.1(−12)	
					50	3.0(06)	8.6(12)	2.1(−12)	
					75	3.1(06)	1.3(13)	3.2(−12)	
H ₂ CO									
HD 163296	H ₂ CO 3 ₁₂ –2 ₁₁	890 ± 89 ^d	33.4	−3.55	25	5.7(06)	2.1(12)	6.3(−12)	< 0.24
					50	6.2(06)	3.0(12)	9.2(−12)	< 0.43
					75	6.4(06)	4.2(12)	1.3(−11)	< 0.50
TW Hya	H ₂ CO 3 ₁₂ –2 ₁₁	291 ± 29 ^e	33.4	−3.55	25	5.7(06)	3.7(12)	8.9(−13)	1.27 ± 0.13
					50	6.2(06)	5.3(12)	1.6(−12)	1.62 ± 0.16
					75	6.4(06)	7.5(12)	1.8(−12)	1.73 ± 0.17

Notes. The format $a(b)$ translates to $a \times 10^b$. Flux errors are dominated by systematic uncertainties, taken to be 10%.

^(†) Upper limits are derived at the 3σ level using the HD 163296 Keplerian mask (see Section 3).

^(††) Ratios are determined using the CH₃OH disk-integrated column density from Table 2. HD 163296: based on the strictest upper limit from the CH₃OH 2₁₁–2₀₂ (A) line. TW Hya: based on the stacked CH₃OH detection.

^(*) The stacked detection consists of three CH₃OH transitions: CH₃OH 2₁₁–2₀₂ (A) at 304.208 GHz, CH₃OH 3₁₂–3₀₃ (A) at 305.472 GHz, and CH₃OH 4₁₃–4₀₄ at 307.166 GHz. Excitation parameters for the CH₃OH 3₁₂–3₀₃ (A) line are used to calculate column density.

References: ^(a) Rabli & Flower (2010); ^(b) Wiesenfeld & Faure (2013); ^(c) Walsh et al. (2016); ^(d) Qi et al. (2013); ^(e) Öberg et al. (2017).